

行政院國家科學委員會補助專題研究計畫成果報告

The system of early transition metal complexes containing substituted pyrrole—synthesis, characterization, and application in olefin polymerization

計畫類別：x 個別型計畫 整合型計畫

計畫編號：NSC89 - 2113 - M - 018 - 010 -

執行期間：89 年 08 月 01 日至 90 年 07 月 31 日

計畫主持人：黃瑞賢

共同主持人：

本成果報告包括以下應繳交之附件：

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執行單位：國立彰化師範大學化學系(所)

中 華 民 國 90 年 09 月 02 日

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中文摘要

取一倍量的 $\text{Li}\{\text{C}_4\text{H}_2\text{N}(\text{CH}_2\text{NMe}_2)_{2-2,5}\}$ 或者是二倍量的 $\text{Li}\{\text{C}_4\text{H}_3\text{N}(\text{CH}_2\text{NMe}_2)_2\}$ 與氯化鋁在 -78°C ，以乙醚為溶劑的情況下可生成 $\text{AlCl}_2\{\text{C}_4\text{H}_2\text{N}(\text{CH}_2\text{NMe}_2)_{2-2,5}\}$ 【1】及 $\text{AlCl}\{\text{C}_4\text{H}_3\text{N}(\text{CH}_2\text{NMe}_2)_2\}_2$ 【2】此二種錯化合物。將化合物 1 在乙醚中用甲基鋰進行烷基化反應，則可生成二甲基鋁錯化合物 3。化合物 2 熱不穩定，在 CHCl_3 中加熱至 80°C 二天後，會變成未知的化合物。化合物 1,2,3 均有完整的 NMR 光譜圖以及 X-ray 的結構測定。

關鍵詞：氯化鋁、

Abstract

Reactions of AlCl_3 with one equiv of $\text{Li}\{\text{C}_4\text{H}_2\text{N}(\text{CH}_2\text{NMe}_2)_{2-2,5}\}$ or two equiv of $\text{Li}\{\text{C}_4\text{H}_3\text{N}(\text{CH}_2\text{NMe}_2)_2\}$ in diethyl ether at -78°C afforded $\text{AlCl}_2\{\text{C}_4\text{H}_2\text{N}(\text{CH}_2\text{NMe}_2)_{2-2,5}\}$ **1** and $\text{AlCl}\{\text{C}_4\text{H}_3\text{N}(\text{CH}_2\text{NMe}_2)_2\}_2$ **2**, respectively. Alkylation of **1** with MeLi in diethyl ether generates the aluminum dimethyl complex **3**. Compound **2** is thermally unstable and was converted to uncharacterized product in CHCl_3 within two days at 80°C . Compounds **1**, **2**, and **3** were characterized by NMR spectroscopy and X-ray structure determination. Keywords: aluminum, pyrrole, Alkylation

Introduction

Lewis acidic aluminum halide or alkyl compounds, AlX_3 or AlR_3 , have been observed to form simple adducts with Lewis bases, such as amines¹ and ethers,² which normally adopt a monomeric, four-coordinate tetrahedral geometry. Similarly, the use bi- and tridentate ligands, such as aryl amines,³ bifunctional, multi-dentate phenolates,⁴ multi-dentate amides,⁵ and amidophosphines,⁶ in the preparation of high-coordinate group 13 metal complexes has seen widespread popularity.

Our investigations have noted that mono-anionic, bi- and tridentate pyrrole ligands containing dimethylamino part(s) type ligand, $\{\text{C}_4\text{H}_3\text{N}(\text{CH}_2\text{NMe}_2)_2\}^-$ and $\{\text{C}_4\text{H}_2\text{N}(\text{CH}_2\text{NMe}_2)_{2-2,5}\}^-$, were first synthesized in 1947^{7a}. However, very few examples of organometallic complexes containing this bi- or tridentate ligands have been reported. In fact, thus far, only one compound, involving the monoanionic,

bidentate ligand bound to a chromium atom, has been identified using X-ray diffraction.⁷

In continuing our efforts in the chemistry of substituted pyrrolate compounds of early transition metals, we have focused our attention to group 13. Herein, we report the chemistry of aluminum chloride with bi- and tridentate substituted pyrrolate ligands.

Results and Discussion

The reactions of AlCl_3 with $\{\text{C}_4\text{H}_3\text{N}(\text{CH}_2\text{NMe}_2)_2\}^-$ and $\{\text{C}_4\text{H}_2\text{N}(\text{CH}_2\text{NMe}_2)_{2-2,5}\}^-$ are summarized in Scheme 1.

Scheme 1 here

Compound **1** was prepared in 84% yield by reacting AlCl_3 and one equiv. of $\text{Li}\{\text{C}_4\text{H}_2\text{N}(\text{CH}_2\text{NMe}_2)_{2-2,5}\}$ in diethyl ether at -78°C . The five-coordinate aluminum compound **1** shows a geometry in solution that is consistent with meridional bonding of the $\{\text{C}_4\text{H}_2\text{N}(\text{CH}_2\text{NMe}_2)_{2-2,5}\}^-$. The methylene protons of **1** give rise to a sharp singlet in the proton NMR spectrum at 3.68 ppm. Similar proton NMR spectral patterns have been observed for analogous Ti^8 and Zr^9 derivatives with $\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_{2-2,5}\}^-$ as the ancillary ligand. The ^{13}C gated-decoupling NMR spectrum shows a triplet for the methylene carbon at 60.6 ppm with a normal sp^3 coupling constant at 137 Hz. A crystal obtained from a saturated methylene chloride/diethyl ether solution of compound **1** was characterized by single crystal X-ray structure analysis. The crystallographic data are summarized in Table 1. Selected bond distances and angles are listed in Table 2, and an ORTEP plot is depicted in Figure 1.

Compound **1** is best described as distorted trigonal bipyramidal with the tridentate monoanionic $\{\text{C}_4\text{H}_2\text{N}(\text{CH}_2\text{NMe}_2)_{2-2,5}\}^-$ attached to aluminum in a meridional geometry. The pyrrolate nitrogen atom is σ -bonded to aluminum with an Al-N distance of 1.827(3) Å which is approximately 0.4 Å shorter than the mean bond distance of the dimethylamino nitrogen atoms coordinated to aluminum. The two dimethylamino nitrogen atoms occupy axial positions while the pyrrolate nitrogen and two chlorides occupy the equatorial positions forming two five member rings with bond angles of N(2)-Al-N(3) and N(2)-Al-N(1) of $77.63(12)^\circ$ and $77.12(12)^\circ$, respectively.

The analogous reaction of AlCl_3 with two equiv.

of $\text{Li}\{\text{C}_4\text{H}_3\text{N}(\text{CH}_2\text{NMe}_2)_2\}$ in diethyl ether at $-78\text{ }^\circ\text{C}$ yielded an off-white compound, $\text{AlCl}\{\text{C}_4\text{H}_3\text{N}(\text{CH}_2\text{NMe}_2)_2\}_2$ **2**, which was isolated in 84% yield. ^1H NMR spectrum of **2** highlights the diastereotopic nature of the methylene protons, showing doublets at 4.10 ppm and 3.79 ppm while the dimethylamino protons give rise to doublets at 2.64 and 2.56 ppm. Crystals of **2** suitable for X-ray structure analysis were obtained from a diethyl ether solution. The crystallographic data are summarized in Table 1. Selected bond distances and angles are listed in Table 2, and an ORTEP plot is depicted in Figure 2.

Similar to **1**, compound **2** can be described as a distorted trigonal bipyramid with the two dimethylamino nitrogen atoms occupying axial positions and with an angle of $170.48(11)^\circ$. The two pyrrolate nitrogen atoms and the chlorine atom form a trigonal plane with the sum of angles $\text{N}(1)\text{-Al-Cl}$, $\text{N}(1)\text{-Al-N}(3)$, and $\text{N}(3)\text{-Al-Cl}$ at nearly 360° . The aluminum to axial nitrogen bond distances (*ca.* 2.1 \AA) are 0.2 \AA longer than aluminum to equatorial nitrogen distance (*ca.* 1.9 \AA), indicating the σ -bonded anionic pyrrolate nitrogen atoms are bound more strongly than are the axial nitrogen atoms which are bonded through lone-pair $\text{N}\rightarrow\text{Al}$ interactions.

Compound **2** is not thermally stable and is converted within two days to uncharacterized products when heated to $80\text{ }^\circ\text{C}$ in deuterated chloroform in an NMR tube under an inert atmosphere. In order to eliminate the possible reaction of compound **2** with chloroform, benzene was used as solvent, and the same result was observed. However, the rate of decomposition of compound **2** in chloroform is much faster than that in benzene. Alkylation of compound **2** by MeLi or *n*-BuLi in diethyl ether was not successful, and $\text{Li}\{\text{C}_4\text{H}_3\text{N}(\text{CH}_2\text{NMe}_2)_2\}$ was recovered.

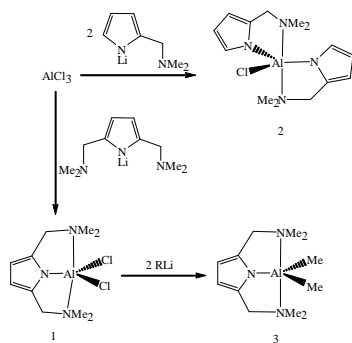
Alkylation of **1** with two equiv. of MeLi afforded $\text{AlMe}_2\{\text{C}_4\text{H}_2\text{N}(\text{CH}_2\text{NMe}_2)_2\}$, **3**, in 85% yield. The ^1H NMR spectrum of **3** is in consistent with a C_{2v} symmetric structure with the two methyl groups observed as singlet in the ^1H NMR spectrum at -0.85 ppm. The region of the ^{13}C NMR spectrum associated with the methyl groups attached to aluminum shows a very weak quartet due to the quadrupole interaction of aluminum ($I=5/2$),¹⁰ which also has a low J_{CH} coupling constant at 111 Hz. Compound **3** is extreme air-sensitive and decomposes rapidly when exposed to the atmosphere. Colorless cube crystals were obtained from saturated diethyl ether solution, and X-ray analysis was performed. Crystallographic data and selected bond distances and angles of compound **3** are summarized in Table 1 and Table 2, respectively. An ORTEP plot of compound **3** is shown in Figure 3.

The structure of the methylaluminum compound **3** is very similar to that of compound **1**, exhibiting a distorted trigonal bipyramidal structure with the two dimethylamino nitrogen atoms occupying axial positions. The pyrrolate nitrogen and the two methyl

groups form a trigonal plane with the sum of bond angles of $\text{N}(2)\text{-Al-C}(1)$, $\text{N}(2)\text{-Al-C}(2)$ and $\text{C}(1)\text{-Al-C}(2)$ at 359.98° . Surprisingly, compound **3** is quite thermally stable in CDCl_3 , showing no decomposition at $70\text{ }^\circ\text{C}$ during 24 h. An attempt to synthesize $\text{AlMeCl}\{\text{C}_4\text{H}_2\text{N}(\text{CH}_2\text{NMe}_2)_2\}$ by reacting **1** with one equiv. of MeLi in diethyl ether resulted in the formation of the dimethyl compound **3** and left unreacted **1**. Moreover, upon mixing equimolar amounts of compounds **1** and **3** in C_6D_6 in an NMR tube fitted with a J. Young adapter and heated to $80\text{ }^\circ\text{C}$ for 3 days, no reaction was observed.

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- Similar phenomena have been seen, for example : Coles, M. P.; Swenson, D. C.; Jordan, R. F.



Scheme 1

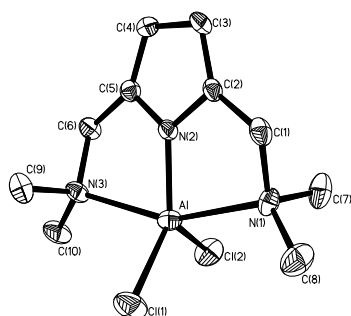


Figure 1

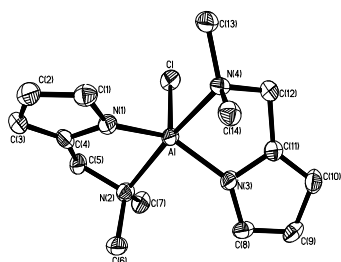


Figure 2

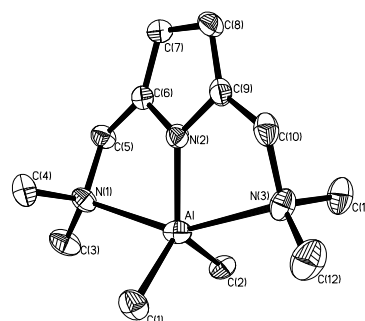


Figure 3

Table 2. Selected Bond Distances (Å) and Angles (°) for compound 1, 2 and 3

1		2		3	
Al-N(2)	1.827(3)	Al-N(3)	1.896(3)	Al-N(2)	1.8617(13)
Al-Cl(1)	2.135(2)	Al-N(1)	1.906(3)	Al-C(1)	1.980(2)
Al-Cl(2)	2.146(2)	Al-N(4)	2.105(3)	Al-C(2)	2.000(2)
Al-N(3)	2.211(3)	Al-N(2)	2.110(3)	Al-N(3)	2.426(2)
Al-N(1)	2.257(3)	Al-Cl2	2.1907(12)	Al-N(1)	2.2838(14)
N(2)-Al-Cl(1)	130.61(11)	N(3)-Al-N(1)	143.93(12)	N(2)-Al-C(1)	126.45(7)
N(2)-Al-Cl(2)	118.20(11)	N(3)-Al-N(4)	81.18(11)	N(2)-Al-C(2)	116.99(6)
Cl(1)-Al-Cl(2)	111.17(6)	N(1)-Al-N(4)	95.66(11)	C(1)-Al-C(2)	116.54(7)

Table 1. Summary of Crystallographic Data for Compounds 1, 2, and 3

	1	2	3
formula	C ₁₀ H ₁₈ AlCl ₂ N ₃	C ₁₄ H ₂₂ AlClN ₄	C ₁₂ H ₂₄ AlN ₃
fw	278.12	308.79	237.32
temp.	150(1) K	150(1) K	150(1) K
wavelength	0.71073 Å	0.71073 Å	0.71073
diffractometer used	SMART CCD	SMART CCD	SMART CCD
crystal system	orthorhombic	orthorhombic	orthorhombic
space group	Pbca	P2 ₁ 2 ₁ 2 ₁	Pbca
a, Å	11.9929(8)	8.4637(2)	12.1410(2)
b, Å	14.6956(9)	9.2139(2)	14.9987(2)
c, Å	15.6033(9)	20.1903(3)	15.6734(1)
volume (Å ³), z	2750.0(3), 8	1574.51(6), 4	2854.11(6), 8
density (Cald., Mg/m ³)	1.344	1.303	1.105
absorp. coeff. (mm ⁻¹)	0.515	0.295	0.124
F(000)	1168	656	1040
crystal size (mm)	0.20x0.15x0.13	0.20x0.20x0.16	0.60x0.60x0.40
θ range (degree)	2.55 to 25.00	2.02 to 26.38	2.52 to 27.50
reflection collected	8595	7497	19162
indep. reflections	2394(Rint=0.0767)	3190(Rint=0.0503)	3266(Rint=0.0266)
absorp. correction	empirical used sadabs	empirical used sadabs	empirical used sadabs
max. and min. trans.	0.9280 and 0.8154	0.9280 and 0.7818	0.9280 and 0.8057
data/restraints/para.	2394/0/146	3190/0/182	3266/0/152
Goodness-of-fit on F ²	1.185	1.056	1.142
final R indices[I>2σ(I)]	R1=0.0726, wR2=0.0949	R1=0.0502, wR2=0.0887	R1=0.0470, wR2=0.1168
R indices (all data)	R1=0.1102, wR2=0.1038	R1=0.0670, wR2=0.0943	R1=0.0526, wR2=0.1198
extinction coeff.	0.0031(5)	0.0033(9)	0.0030(7)
largest. diff. peak and hole	0.343 and -0.260 eÅ ⁻³	0.292 and -0.218 eÅ ⁻³	0.339 and -0.281 eÅ ⁻³
structure determined program	SHELXTL	SHELXTL	SHELXTL